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Patents ADP number *(if you know it)*   ~~2576002~~

If the applicant is a corporate body, give the country/state of its incorporation

United Kingdom   54 51 0012

4.	Title of the invention	Smectic Liquid Crystal Devices

5.	Name of your agent *(if you have one)*	J B Edwards

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12. Name and daytime telephone number of person to contact in the United Kingdom

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PATENT APPLICATION

SMECTIC LIQUID CRYSTAL DEVICES

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File Ref: DERA/HO/COM/IPD01/P2621

15 Filed: 1997

Slippery Surfaces cases:

1   (P2618)general case genslip.1 - cover all the following file on same day

20 2   (P2619)bistable case - bislip1.doc   was pat4 etc involves HP

3.   (P2620)twisted nematic tnslip1.doc improves TN devices was pat5 etc

4   **(P2621)ferro electric   - feslip1.doc   improves FELCDs**

25

SMECTIC LIQUID CRYSTAL DEVICES

This invention relates to smectic liquid crystal devices. for example ferroelectric liquid crystal devices. devices (e.g. displays) with improved contrast and brightness.

antiferroelectric liquid crystal devices. smectic liquid crystal devices. electroclinic liquid crystal devices; electro-optic shutters. spatial light modulators, and displays.

Liquid crystal devices typically comprise of a thin layer of a liquid crystal material contained between cell walls. Optically transparent electrode structures on the walls allow an electric field to be applied across the layer causing a re-ordering of the liquid crystal molecules.

There are three known types of liquid crystal material nematic. cholesteric and smectic each having different molecular ordering. The present invention concerns devices using smectic materials.

There are a number of devices based on smectic liquid crystal materials including:

A: Ferroelectric liquid crystals (usually SmC*).

One example of this is bistable and is often termed surface stabilised FLC devices (SSFLC) ref. N. A. Clark and S. T. Lagerwall. Appl. Phys. Lett.. 36. 899 (1980). In this device planar aligned surfaces are arranged with parallel or anti parallel preferred alignment directions. The device is cooled from an overlying Smectic A phase into a bookshelf arrangement of the smectic layers. that is the material forms into micro layers arranged normal to the cell walls as in books on a shelf.

In the original patent, the device used an unrubbed polymer surface alignment treatment to ensure the liquid crystal director n lies preferentially and substantially parallel to the surface plane (i.e. $\perp$ to s. the surface normal). A preferred direction was then imparted by heating to the smectic A phase and shearing the layers in the required

direction. The layers remained fixed on cooling into the SmC* phase. The surface energy is minimum for **n** $\perp$ **s** so that two minimum energy states occur which can be selected by suitable DC electric field.

5   Bradshaw and Raynes realised that improved SmA alignment for such a device resulted by having a chiral nematic N* phase above the SmA in which the pitch was sufficiently long for the surface forces to cause unwinding of the spontaneous helicity for a significant temperature range above the transition. They also required that the surface should be pre-treated to impart the preferred directions, often by use of parallel

10   or antiparallel rubbing of a polyimide or polyamide layer; GB-2.210.469 USP-4.997.264. GB-2.209,610. USP-5.061.047. GB-2.210.468.

Later it was found that when a bookshelf aligned (where the layer normal is parallel to the plane of the device i.e. $\delta=0$) SmA sample is cooled into the SmC* phase. the layers

15   become tilted in a chevron type of configuration; two type of chevron can exist and are defined as C_1 and C_2 type (ref J.Kanbe et al Ferroelectrics (1991) vol 114. pp3). This has been ascribed to the combined effect of shrinkage of the smectic layer spacing and pinning of the layers at the surface. The resulting chevron structure means that the director in the middle of the cell is (roughly) fixed in one of two orientations

20   significantly less than the full cone angle. This means that with no applied field there is a substantial drop in the angle between the optic axis of the two "surface stabilised" states which leads to a corresponding drop of the display brightness. A number of methods of improving the optical brightness have been proposed for practical devices:

25   1   AC field stabilisation:

An applied AC field pulse of insufficient time and voltage (τ V) to latch into the two states couples to the dielectric tensor (primarily the dielectric biaxiality) to increase the angle between these states and enhance the brightness. The main problem with this type of approach is that a high frequency voltage is required constantly to maintain the

30   required brightness. This causes a high power dissipation. particularly for complex displays where the applied frequency is high. Usually the brightness is compromised

by using a suitably low AC voltage. It has the advantage that. if C2U type alignment is used. there is no need for surface switching. and hence surface memory effects are minimal, and the slower switching at the surface does not effect the device.

5 2 High pre-tilt Parallel:

This geometry has (approximately) the same chevron structure with the director at the chevron interface also at a low angle to the rubbing direction. However. the director at the surface is at a much higher in-plane twist angle due to the competing effects of

10 lying on the SmC* cone and with the preferred alignment pre-tilt. This type of device gives good brightness but suffers from a slower response since it involves surface switching, and from strong surface memory problems which may lead to image sticking.

15 3 Quasi-bookshelf:

Two methods may be used to reduce the layer tilt angle and thereby increase the device brightness. Pre-treating the device with a low frequency field of sufficient magnitude or choosing certain materials in which the layer shrinkage on cooling

20 through the smectic phases is reduced (some materials may actually increase layer spacing on cooling). Such a device has similar advantages and disadvantages to the high pre-tilt configurations.

4 Uniform Tilted layer (High pre-tilt anti-parallel) geometry:

25

Similar to previous two geometry's but there is no chevron (and therefore no constraint on the director at the cell centre) and the high angle between the bistable states is stabilised solely by the surfaces.

30

B: Electro-clinic optical shutters:

Application of a DC field to the smectic A (or other orthogonal smectic) phase of a chiral material leads to an induced tilt of the director and hence optical axis normal to

5   the applied field. In a (approximately) planar aligned liquid crystal cell with electrodes on the substrate surfaces the electroclinic effect induces a rotation of the optic axis by an angle proportional to the applied field E. Thus, an optical shutter with full analogue amplitude or phase modulation may be obtained.

10   A common problem with such a device is obtaining suitably uniform and planar alignment of the smectic layers. A lesser problem is that the induced switching may involve some rotation of the director away from the preferred alignment direction at the surface. This movement is subject to a surface viscosity which may impede the switching time of the device and also to certain surface memory effects.

15

C: Anti-ferroelectric smectic liquid crystals (AFLC):

Certain materials form an anti-ferroelectric phase which may be used in active matrix or direct drive devices. Effectively these devices have a similar appearance to the

20   smectic A phase until sufficient DC voltage is applied, above which the sample is in either of two states (depending on the polarity of the applied signal) similar to the normal ferroelectric phase.

There is a limited number of materials which form this phase (particularly over a wide

25   temperature range) and all those found so far have direct isotropic to smectic phase (i.e. no overlying chiral nematic phase). This means that the materials are more difficult to align, forming batonnets (see Gray and Goodby book) of the smectic at this transition.

30

The mechanism for this is that the smectic layer structure nucleates in a limited number of "cold spots" in the isotropic liquid. The layers then curve around this point to minimise the bend and splay of the layer normal. Where the layers meet the surface they become pinned and difficult to move. Hence, it is difficult to obtain the desired

5 layer arrangement (e.g. planar or bookshelf) once the batonnet structure has pre-formed. On cooling into the AFLC phase, the applied field tends to induce twist of the director at the surfaces which also leads to problems associated with surface switching such as slower speed, surface memory effects, etc.

10 **D: SmC* Optical Shutters:**

Bradshaw and Raynes also described a type of device in which the FLC is obtained from cooling directly from the unwound N* phase in a parallel rubbed device, preferably with in applied DC field applied during the phase transition. The unwound

15 N* phase has the director in the rubbing directions and on cooling into the SmC* this orientation is maintained and the layer normal twists through the angle θ. Degeneracy of the direction in which the layer normal is oriented is removed by the application of the DC field.

20 This is a monostable device, since it always relaxes back to the surface stabilised state (with n $\parallel$ s) once the field is removed (it may be used in devices when the field is retained, either through AC stabilisation or through inclusion of TFTs or similar non-linear electrical elements at each pixel. However, it is fast (due to Ps). Primarily switching occurs in the bulk of the cell and little or no switching occurs at the surface.

25 However, this means that the director is highly twisted and non uniform structure. This means that the optical appearance is poor (particularly if used in conjunction with a dye as done in early Hitachi work) and so this is a case where surface switching is required to improve performance. Also, alignment is difficult over a wide temperature range because layer shrinkage still occurs in many N-SMC* materials, leading to a

30 chevron structure and associated defects.

According to this invention, problems in the above devices may be reduced by use of a surfactant to lower the interaction between the surface(s) of cell wall(s) and the liquid crystal in the smectic phase, or in the overlying nematic phase from which the cell is cooled into the smectic phase for all operating temperatures. This use of a surfactant may be termed a slippery surface treatment. Thus improved alignment, optical properties, switching speed and stability to shock of smectic devices are achieved through slippery surface treatment.

According to this invention a smectic liquid crystal device comprises:

a liquid crystal cell including a layer of smectic liquid crystal material contained between two walls bearing electrodes and surface treated to give both an alignment and a surface tilt to liquid crystal molecules:

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means for reducing anchoring energy at the surface alignment on one or both cell walls.

The means for reducing anchoring energy may be an oligomer containing esters, thiols, and/or acrylate monomers and or which is either spread on the surface or added to the liquid crystal material.

In its most elemental form the surfactant provides a slippery surface which reduces the interaction between the liquid crystal molecules and those of the surface of the cell wall (or alignment layer surface). Thus, the slippery surface may be thought as having

5 increased freedom for translational and rotational movement of the liquid crystal molecules closest to the surface. There are five surface terms (ref: Int Ferroelectric Liquid Crystal Conf (FLC95), Cambridge, UK, 23-27 July 1995, vol.178 No.1-4 J.C.Jones, pp155-165) which are relevant and may be controlled by the surfactant:

10 (1) α, zenithal anchoring energy. How easily the director surface tilt angle is changed (i.e. a rotational energy).

(2) β, azimuthal anchoring energy - case of changing surface twist angle of director (i.e. a rotational energy)

15

(3) γ, related to the pretilt angle of the director at the surface

(4) Layer pinning term - How easily layers may be moved across the surface (i.e. a translational energy). This is the macroscopic effect of the (partial) adsorption of

20 liquid crystal molecules onto the surface layer reducing translational movement of the molecules and hence of the smectic layers.

(5) Polar surface energy - In ferroelectrics (or flexoelectrics) a term which is minimum for a particular orientation of the Ps at the surface.

25

In the present invention each of these factors is influenced by the presence of a slippery surfactant which acts to separate the solid and liquid crystal regions by the induced changes of liquid crystal order close to the surface. For example, if nematic order exists close to the surface layer of a smectic device, then layer pinning is greatly

30 reduced. If the cone angle is lower surface switching is reduced as

will the polar surface term.

Advantages provided by the present invention:

(1)   Reduced layer pinning hence control of the smectic layers is easier:

(2)   Reduced nematic-like surface energies. hence orientation changes of the director at the surface are enhanced.

(3)   Reduced adsorption of liquid crystal molecules at the surface. hence reduced surface memory effects and reduced surface viscosity:

(4)   Reduced polarity of the surface. hence less coupling to the spontaneous polarisation coefficient (Ps) in ferro electric liquid crystal systems resulting in less T state formation.

Brief description of drawings.

The invention will now be described. by way of example only with reference to the accompanying drawings of which:-

Figure 1 is a diagrammatic view of a bistable ferro electric display with row and column drivers providing an x.y matrix display:

Figure 2 is a cross section of the display cell of Figure 1:

Figure 3 is a schematic view of a layer of ferro electric liquid crystal material. showing two alignment configurations. the C_1 and the C_2 states:

Figure 4 is a schematic view showing the two switched states of the display of Figure 1: and

Figure 5 is a graph of memory angle against applied voltage for a cell containing a standard material. and the same material but including a slippery surface additive.

Detailed description of invention.

The display cell 1 shown in Figures 1, 2 comprises two glass walls 2, 3 spaced about

5   1-6 μm apart by a spacer ring 4 and/or distributed spacers.

Electrode structures 5, 6 of transparent tin oxide are formed on the inner face of both walls. These electrodes are shown as row and column forming an X, Y matrix but may be of other forms. For example, radial and curved shape for a polar co-ordinate

10   display, or of segments form for a digital seven bar display, or plain sheet electrodes to form an optical shutter.

A layer 7 of smectic liquid crystal material is contained between the walls 2, 3 and spacer ring 4.

15

Polarisers 8, 9 are arranged in front of and behind the cell 1. Row 10 and column 11 drivers apply voltage signals to the cell. Two sets of waveforms are generated for supplying the row and column drivers 10, 11. A strobe waveform generator 12 supplies row waveforms, and a data waveform generator 13 supplies ON and OFF

20   waveforms to the column drivers 11. Overall control of timing and display format is controlled by a control logic unit 14.

Prior to assembly, the walls 2, 3 are surface treated by spinning on a thin layer of polymeric material such as polyimide or polyamide, drying and where appropriate

25   curing; then buffing with a soft cloth (e.g. rayon) in a single direction R_1, R_2. This known treatment provides a surface alignment for liquid crystal molecules. In the nematic and cholesteric phases and in the absence of an applied electric field the molecules at the surface walls 2, 3 align themselves along the rubbing direction R_1, R_2 and at a pretilt angle ξ of about e.g. 2° to 10° to the surface.

The surface alignment treatment is arranged to provide the required value of pretilt ξ. For example the material polyimide (e.g. Polyimide 32) when rubbed gives a typical pretilt of about 2°; the actual value depends upon liquid crystal material and the

5   processing. Alternatively. as described in GB-A-2.286: GB-A-2.286.467: GB-A-2.286.894: GB-A-2.2986.893, the cell walls may have formed thereon grating structures which provide a range of pretilt angles and alignment directions. The gratings may be symmetric and/or asymmetric in profile. and shaped to give any desired value of pretilt ξ. and azimuthal and zenithal anchoring energies β, α

10   respectively.

The device may operate in a transmissive or reflective mode. In the former light passing through the device e.g. from a tungsten bulb 15 is selectively transmitted or blocked to form the desired display. In the reflective mode a mirror 16 is placed

15   behind the second polariser 9 to reflect ambient light back through the cell 1 and two polarisers. By making the mirror 16 partly reflecting the device may be operated both in a transmissive and reflective mode.

Pleochroic dyes may be added to the material 7. In this case only one polariser is

20   needed and the layer thickness may typically be 4-10μm.

If the smectic material 7 is a chiral smectic e.g. smectic C (S_C^*) then a bistable device can be made. Such a device is the surface stabilised ferroelectric device (SSFLC) supporting two bistable states which are optically distinct. In a chiral smectic material

25   molecules tend to lie and move along the surface of an (imaginary) cone as shown in Figure 4. When the surface alignment directions R1. R2 are parallel the (z) axis of these cones are parallel to these alignment directions and the molecules lie either side of the axis on the cone surface.

In one switched state D1 the molecules lie on one side of the cone. and in the second bistable state D2 lie on the other side of the cone. The switching is achieved by application of a voltage pulse of appropriate sign and length applied through the electrodes 6, 7 coupling with a spontaneous polarisation coefficient Ps of the material. The cone angle, θ_c, is a function of material parameters. In devices the molecules in their two switched positions D1, D2. do not lie on the extremities of the cone but some small distance away. This means that the angle between the bistable positions is somewhat less than the cone angle. and can be increased a bit by application of an ac voltage signal to the material; this is known as ac stabilisation mentioned above. Ideally the angle between the switched states is 45° because this would allow maximum contrast for the cell when arranged between crossed polarisers 8, 9 with the axis of one polariser along one of the switched directions. This gives a dark state in one switched position and a light state in the other switched position.

The angular distance between the two state is defined as the memory angle. θ_m (see N. Itoh et al, Jpn. J. Appl. Phys., **31**, L1089 (1992)). The optimum memory angle for maximum brightness in the light state is therefore 45°. However most materials possess a memory angle which is much less than 45° and so suffer from loss in brightness.

A weak anchoring treatment can be added to a ferroelectric to increase the memory angle and so improve the display brightness.

Example of cell preparation.

Alignment surfaces were prepared by spin coating a layer of probomide 32 (Ciba

5   Geigy) onto ITO coated glass and baking the substrates at 300°C. The surfaces were

then rubbed in one direction R by a nylon cloth attached to a rotating roller. Finally

cells were constructed in which the rubbing direction R_1 on one surface was parallel to

that R_2 on the other. The cell gap (d) was set to 1.1 μm using monodispersed spacer

beads in the edge seal. Each cell was then filled with ZLI 5014 (Merck) ferroelectric

10   liquid crystal doped with small percentages of N65. Before filling the N65 was cured

in a separate cell.

Figure 5 shows the memory angle measured from two cells containing either pure ZLI

5014. or 4% N65 in ZLI 5014 as a function of applied voltage (50kHz AC). The

15   results clearly show that the weak anchoring treatment has lead to a significant

increase in memory angle at all voltages. Therefore the treatment has improved this

ferroelectric device by increasing the on state transmission between crossed polarisers.

For example at 5 V, the memory angle has increased from 17.1° to 34.4° which would

lead to a device which is 3.7 times brighter.

20

Bistable ferro electric devices switch upon receipt of a unidirectional pulse of

appropriate direction. amplitude. and length. Strobe pulses are applied sequentially

down the rows. whilst one of two different data pulses are applied to each column.

Examples of addressing are described in USP-5.497.173. GB-2.232.802: US Serial

25   No. 07/977.442. GB-2.262.831.

Several other smectic devices may be made with alignment surfaces of the present invention. For examples electro-clinic smectic devices: mono stable ferro electric devices USP-5,061,047, USP-4,969,719, USP-4,997,264, colour change smectic

5   projection cells USP-5,189,534, GB-2,236,403. The alignment may produce a chevron type C1 or C2 type of smectic micro layer arrangement; or a tilted bookshelf arrangement where rubbing directions on opposite walls are in the same direction, or real bookshelf alignment.

10   Reducing anchoring energy allows small amounts of translational movement to occur in micro layers formed during cooling from isotropic phases to smectic phases.

Reduction of anchoring energy can be applied to various smectic devices as follows:

15   (i). Bookshelf and Quasi-bookshelf with low surface viscosity and no surface memory effects

Most materials used in FLC devices exhibit layer shrinkage on cooling through the SmC* phase due to the increase of the angle between the molecules and layer normal

20   on cooling. The tendency for the pinning of the smectic layers at the surfaces then leads to the formation of a chevron structure.

If the pinning energy is sufficiently high to prevent any translational slippage of the layers (i.e. the energy cost associated with layer slippage is much greater than energies

25   associated with the chevron interface, elastic distortion of the director in the triangular director profile, and the orientational surface energy associated with the director being unable to lie in the preferred alignment direction) the layer shrinking requires that the layers tilt with respect to the surface normal.

If both surfaces have similarly high layer slipping terms then the layers must tilt into a chevron structure which is necessarily symmetric about the central plane of the cell. For typical materials this degree of layer shrinkage is such that the layer tilt angle δ is

5   a constant fraction of the smectic cone angle θ usually about $\delta/\theta = 0.85$. This causes a reduction in the angle between the two bistable states and hence optical contrast in the cell. A higher memory angle may be achieved by lowering δ in what is often termed quasi bookshelf geometry. If the layer pinning term is made sufficiently weak (for example a relatively high concentration of the surfactant is used) a bookshelf geometry

10   is obtained i.e. $\delta = 0$. If the azimuthal angle β is also made sufficiently low then a uniform director profile is possible in which the two bistable states are at the optimum angle of $\pm\theta$ to the rubbing direction. The resulting high contrast and brightness of the display is also combined with the other advantages of reduced/no surface memory effects (which would be a problem in other bookshelf devices) and faster response

15   (due to the decoupling of the surface director from the solid surface the surface viscosity becomes equivalent to that of the bulk).

(ii). Chevron with improved memory angle.

20   This device uses the slippery surfactant at sufficient concentration to lower layer tilt angle in chevron geometry, thereby leading to a higher memory angle and improved brightness for multiplexed devices. However. it may be possible to lower the orientational surface energies without a strong effect on the translation energy (i.e. layer pinning). Thus. the chevron structure would remain to a large extent (i.e. δ

25   remains unchanged) but the orientation of the director at the surface would be higher. For no applied AC field the surface twist of the director would approach that of the chevron interface. The optical uniformity of this state (and hence contrast) would be improved. Moreover. the lowered surface energy would increase the angle of the director at the surface with an applied AC field. and thus the brightness of an AC

30   stabilised display will also be enhanced.

(iii). Improving isotropic to smectic transition.

Surfactant allows layers to slip easily over the surface to form energy state (i.e.
uniform layers) dictated by orientational properties of the surface alone (i.e. no
translational restrictions). Particularly useful also in AFLC where N* (cholesteric)
phase is usually not apparent, but also in other devices (e.g.. FLC) where stringent
material requirements prevent the use of an N(*) phase.

(iv)..Improved stability to mechanical, triennial or electrical damage of smectic
devices.

Disruption of a well aligned smectic sample through mechanical, electrical or thermal
shock leads to pinning of the layers at the surface which is difficult to remove. even
though the disrupted state is not the lowest energy state. It' the pinning is removed
then the system may relax back to this minimum energy state before the disruption.

(v)..Improved high tilt chevron device.

High surface pre-tilts are used to ensure that the surface orientation of a FLC device in
the chevron geometry approaches the cone angle and hence the memory angle is
improved (this is used by CANON and is in Jones. Towler Hughes review). In the
unwound N* phase the director has a large degree of splay and bend distortion. On
cooling into the smectic A phase this bend cannot be supported. due to the presence of
the layers and the distortion is pushed to the surfaces where the director is forced to lie
away from the desired pretilt. This may lead to variations in the alignment and hence
defects in the SmC* phase (until switched this geometry often forms a "sandy texture"
on first cooling). Moreover, there may be a plastic change of the pre-tilt caused by the
zenithal surface memory effect. This means that when cooled into the SmC* phase the
effective pretilt is lowered and the resulting memory angle is reduced somewhat.

With the slippery surfactant. the surface memory is reduced and the pre-tilt remains unchanged. Note. this is an example where the slippery surface technique is used in the nematic phase. but results in improved performance of a smectic device.

5   (vi). Improved Electroclinic and antiferroelectric (AFLC) devices

In both of these devices. director twist is induced by the DC electric field there is a tendency for the smectic layers to shrink. If pinned at the surface the applied field tends to induce layer tilt. (although in contradiction to the requirement that $E \parallel Pi$)

10   which reduces optical appearance through defects. and may also reduce viewing angle since the director may tilt out of the cell plane. With the slippery surfactant. both the director and the layers can move easily across the surface. without surface memory or viscosity effects.

15   (viii. Improved N - SmC device.

Advantages ranging from: reduced tendency to form chevron type structure: reduced surface memory; faster surface switching.

20   (viii). Reduced tendency form T state formation in FLC

Due to reduced polar surface interaction. This ensures the good optical and electro-optical properties of any of the above devices (in particular the chevron and bookshelf devices).

25

(ix). Improved alignment of smectic devices.

Treatment prevents defects (for example pitch lines in overlying N^* phase. or Cl state/zig-zags in SmC^*) from become pinned at surface irregularities.

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The monomer materials used may include the following, which are given only by way of example:

methyl acrylate

ethyl acrylate

propyl acrylate

butyl acrylate

pentyl acrylate

2-methylbutyl acrylate

hexyl acrylate

heptyl acrylate

octyl acrylate

nonyl acrylate

decyl acrylate

ethyl hexyl acrylate

methyl methacrylate

ethyl methacrylate

propyl methacrylate

butyl methacrylate

pentyl methacrylate

2-methylbutyl methacrylate

hexyl methacrylate

heptyl methacrylate

octyl methacrylate

nonyl methacrylate

decyl methacrylate

ethyl hexyl methacrylate

styrene

ethylene glycol diacrylate

1,2-propylene glycol diacrylate

propane-1,3-diol diacrylate

butane-1,4-diol diacrylate

pentane-1,5-diol diacrylate

hexane-1,6-diol diacrylate

heptane-1,7-diol diacrylate

octane-1,8-diol diacrylate

nonane-1,9-diol diacrylate

decane-1,10-diol diacrylate

glycerol triacrylate

trimethylolpropane triacrylate

pentaerythritol triacrylate

pentaerythritol tetraacrylate

di-pentaerythritol hexaacrylate

ethylene glycol dimethacrylate

1,2-propylene glycol dimethacrylate

propane-1,3-diol dimethacrylate

butane-1,4-diol dimethacrylate

pentane-1,5-diol dimethacrylate

hexane-1,6-diol dimethacrylate

heptane-1,7-diol dimethacrylate

octane-1,8-diol dimethacrylate

nonane-1,9-diol dimethacrylate

decane-1,10-diol dimethacrylate

glycerol trimethacrylate

trimethylolpropane trimethacrylate

pentaerythritol trimethacrylate

pentaerythritol tetramethacrylate

di-pentaerythritol hexamethacrylate

A further class of polymers includes di-thiol/diene polymers prepared by the copolymerisation of difunctional alkenes with difunctional thiols under free radical conditions. Monofunctional and/or polyfunctional alkenes and/or thiols may be incorporated in order to modify the properties of the polymer, for example to reduce

5   the molecular weight of the polymer or to introduce a controlled degree of crosslinking in the polymer. The following materials given by way of example only may be included in polymers suitable for the subject of the invention:

methyl acrylate	styrene
ethyl acrylate	ethylene glycol diacrylate
propyl acrylate	1,2-propylene glycol diacrylate
butyl acrylate	propane-1,3-diol diacrylate
pentyl acrylate	butane-1,4-diol diacrylate
2-methylbutyl acrylate	pentane-1,5-diol diacrylate
hexyl acrylate	hexane-1,6-diol diacrylate
heptyl acrylate	heptane-1,7-diol diacrylate
octyl acrylate	octane-1,8-diol diacrylate
nonyl acrylate	nonane-1,9-diol diacrylate
decyl acrylate	decane-1,10-diol diacrylate
ethyl hexyl acrylate	glycerol triacrylate
methyl methacrylate	trimethylolpropane triacrylate
ethyl methacrylate	pentaerythritol triacrylate
propyl methacrylate	pentaerythritol tetraacrylate
butyl methacrylate	di-pentaerythritol hexaacrylate
pentyl methacrylate	ethylene glycol dimethacrylate
2-methylbutyl methacrylate	1,2-propylene glycol dimethacrylate
hexyl methacrylate	propane-1,3-diol dimethacrylate
heptyl methacrylate	butane-1,4-diol dimethacrylate
octyl methacrylate	pentane-1,5-diol dimethacrylate
nonyl methacrylate	hexane-1,6-diol dimethacrylate
decyl methacrylate	heptane-1,7-diol dimethacrylate

ethyl hexyl methacrylate

ethylene glycol divinyl ether

1,2-propylene glycol divinyl ether

propane-1,3-diol divinyl ether

butane-1,4-diol divinyl ether

pentane-1,5-diol divinyl ether

hexane-1,6-diol divinyl ether

heptane-1,7-diol divinyl ether

octane-1,8-diol divinyl ether

nonane-1,9-diol divinyl ether

decane-1,10-diol divinyl ether

glycerol trivinyl ether

trimethylolpropane trivinyl ether

divinyl benzene

butane-1,3-diene

pentane-1,4-diene

hexane-1,5-diene

heptane-1,7-diene

octane-1,7-diene

nonane-1,8-diene

decane-1,9-diene

ethylene glycol dithioglycollate

1,2-propylene glycol dithioglycollate

propane-1,3-diol dithioglycollate

butane-1,4-diol dithioglycollate

pentane-1,5-diol dithioglycollate

hexane-1,6-diol dithioglycollate

heptane-1,7-diol dithioglycollate

octane-1,8-diol dithioglycollate

nonane-1,9-diol dithioglycollate

decane-1,10-diol dithioglycollate

octane-1,8-diol dimethacrylate

nonane-1,9-diol dimethacrylate

decane-1,10-diol dimethacrylate

glycerol trimethacrylate

trimethylolpropane trimethacrylate

pentaerythritol trimethacrylate

pentaerythritol tetramethacrylate

di-pentaerythritol hexamethacrylate

ethylene glycol diallyl ether

1,2-propylene glycol diallyl ether

propane-1,3-diol diallyl ether

butane-1,4-diol diallyl ether

pentane-1,5-diol diallyl ether

hexane-1,6-diol diallyl ether

heptane-1,7-diol diallyl ether

octane-1,8-diol diallyl ether

nonane-1,9-diol diallyl ether

decane-1,10-diol diallyl ether

glycerol triallyl ether

trimethylolpropane triallyl ether

di-allyl malonate

di-allyl succinate

di-allyl glutanate

di-allyl hexane-1,6-dicarboxylate

di-allyl keptane-1,7- dicarboxylate

di-allyl octane-1,8- dicarboxylate

di-allyl nonane-1,9- dicarboxylate

di-allyl decane-1,10- dicarboxylate

di-allyl undecane-1,11- dicarboxylate

di-allyl dodecane-1,12- dicarboxylate

di-allyl phthalate

glycerol trithioglycollate

trimethylolpropane trithioglycollate

pentaerythritol trithioglycollate

pentaerythritol tetrathioglycollate

di-pentaerythritol hexathioglycollate

4,4'-thiobisbenzenethiol

di-allyl iso-phthalate

di-allyl terephthalte

ethane dithiol

propane dithiol

butane dithiol

pentane dithiol

hexane dithiol

heptane dithiol

octane dithiol

nonane dithiol

decane dithiol

undecane dithiol

dodecane dithiol

ethylene glycol di-3-mercaptopropionate

1.2-propylene glycol di-3-mercaptopropionate

propane-1.3-diol di-3-mercaptopropionate

butane-1.4-diol di-3-mercaptopropionate

pentane-1.5-diol di-3-mercaptopropionate

hexane-1,6-diol di-3-mercaptopropionate

heptane-1.7-diol di-3-mercaptopropionate

octane-1.8-diol di-3-mercaptopropionate

nonane-1.9-diol di-3-mercaptopropionate

decane-1,10-diol di-3-mercaptopropionate

glycerol tri-3-mercaptopropionate

trimethylolpropane tri-3-mercaptopropionate

pentaerythritol tri-3-mercaptopropionate

pentaerythritol tetra-3-mercaptopropionate

di-pentaerythritol hexa-3-mercaptopropionate

Also commercial polymers from Norland and Merck eg Norland 65. Norland 63 and Merck MXM035

Claims.

1. A smectic liquid crystal device comprising:

5   a liquid crystal cell including a layer of smectic liquid crystal material contained between two walls bearing electrodes and surface treated to give both an alignment and a surface tilt to liquid crystal molecules:

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means for reducing anchoring energy at the surface alignment on one or both cell walls.

2. The device of claim 1 wherein the means for reducing energy is an oligomer or
15   short chain polymer within the liquid crystal material at the cell walls.

3. The device of claim 1 wherein the means for reducing energy is an oligomer containing esters, thiols, and/or acrylate monomers within the liquid crystal material at the cell walls.

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4. The device of claim 2 wherein the oligomer or short chain polymer has imperfect solubility in the liquid crystal material.

5. The device of claim 2 wherein the oligomer or short chain polymer has a physical
25   affinity for the surface of the cell wall.

6. The device of claim 2 wherein the oligomer or short chain polymer retains a substantially liquid like surface at the polymer and liquid crystal material interface

7. The device of claim 2 wherein the oligomer or polymer is substantially non-crystalline within the liquid crystal material.

8. The device of claim 1 wherein the oligomer or polymer reduces the liquid crystal material order parameter at or adjacent the cell walls.

9. The device of claim 1 wherein the oligomer or polymer changes the phase of the liquid crystal material at or adjacent the cell walls.

10. The device of claim 1 wherein the liquid crystal material is a chiral smectic material, the alignment directions on the two cell walls are substantially parallel, and the device is a bistable device.

12. The device of claim 1 wherein the alignment directions on the two cell walls are non parallel.

13. The device of claim 1 wherein the liquid crystal material is a non-chiral smectic material.

14. The device of claim 1 wherein the liquid crystal material is a smectic A material.

15. The device of claim 1 wherein the alignment is provided by a grating surface.

16. The device of claim 1 wherein the alignment is provided by a rubbed polymer surface.

17. The device of claim 1 wherein one cell wall has an alignment treatment, the other cell wall has no azimuthal alignment direction, and both cell walls are treated with the means for reducing anchoring energy.

Abstract.

Smectic liquid crystal devices are formed by a layer of a smectic liquid crystal material enclosed between two cell walls, both carrying electrode structures, and one or both walls treated to align molecules of the liquid crystal material. Most alignment treatment give alignment and surface pretilt with a strong azimuthal and zenithal anchoring energy to contacting liquid crystal molecules. The invention improves the performance of smectic devices by use of a surfactant to lower the interaction and anchoring energy between the surfaces of the cell walls and the liquid crystal in the smectic phase. The reduction of anchoring energy is achieved by an oligomer or short chain polymer which is either spread on the surface or added to the liquid crystal material. The polymer may be formed by polymerisation of reactive low molecular weight materials in solution in the liquid crystal fluid. Typically up to about 10% of an oligomer is added to the liquid crystal material and cured: either in the cell after filling, or prior to installation in the cell. Various types of smectic devices may be provided; e.g. bistable ferro electric devices, electro clinic devices, and antiferro electric devices.
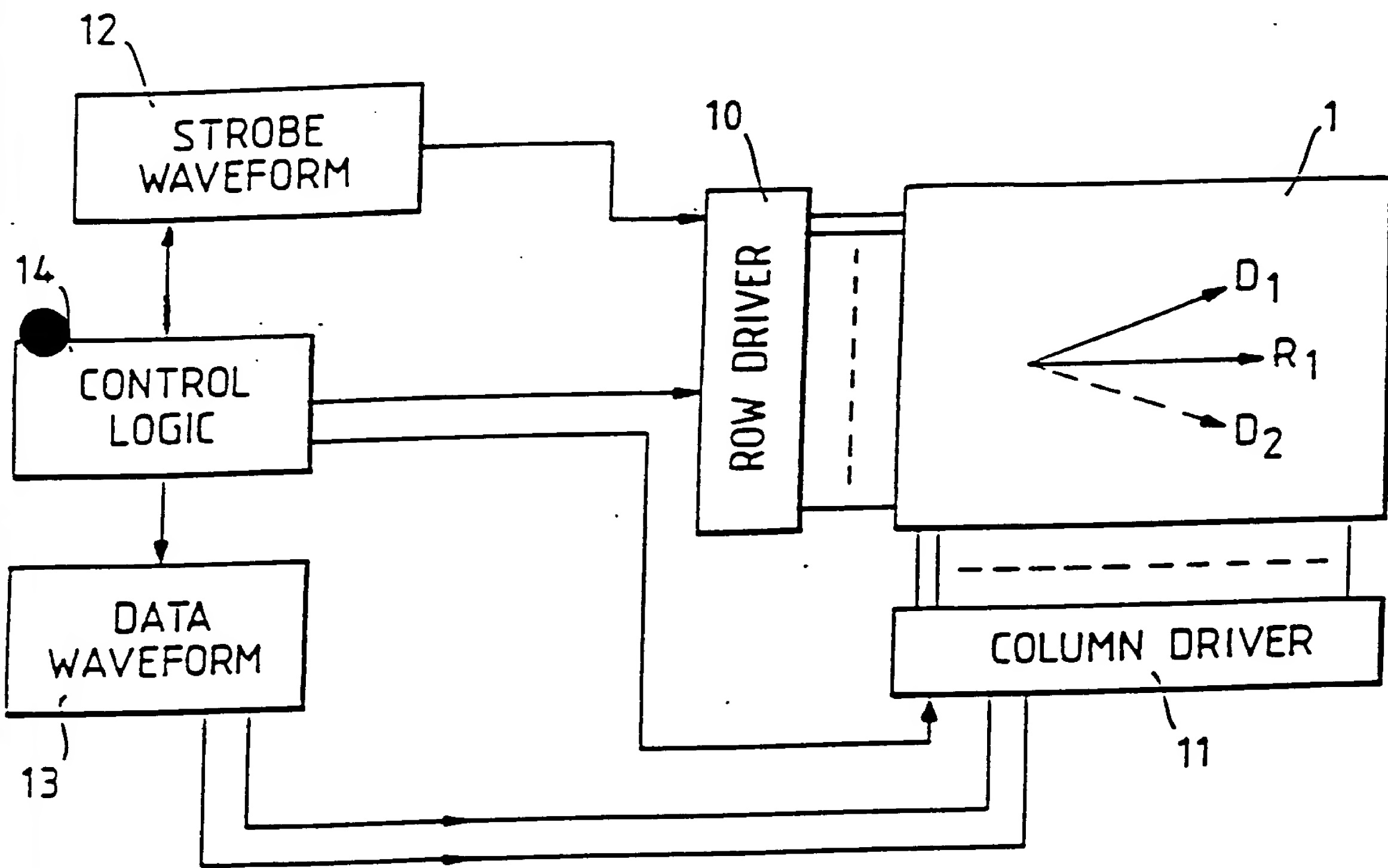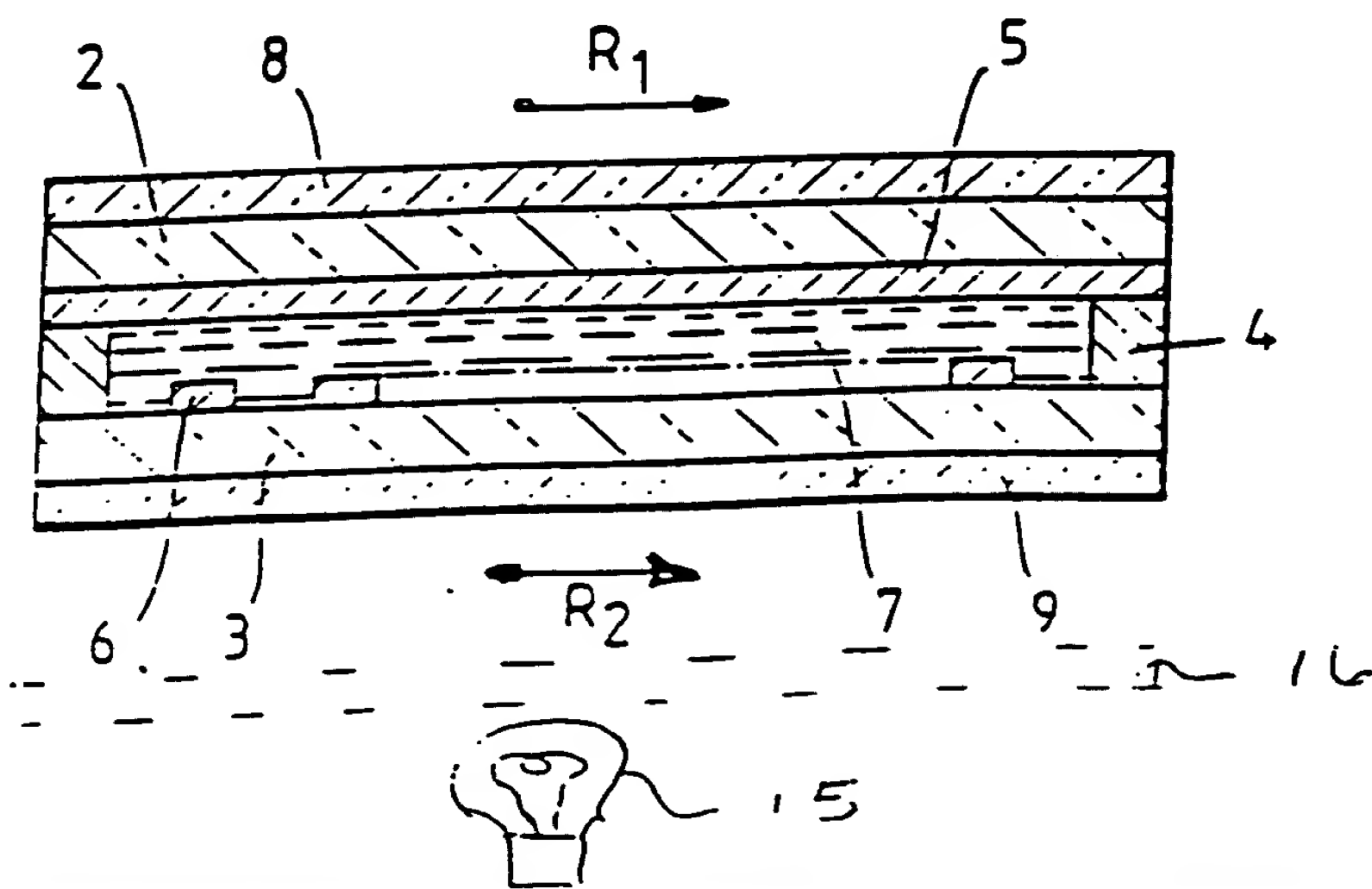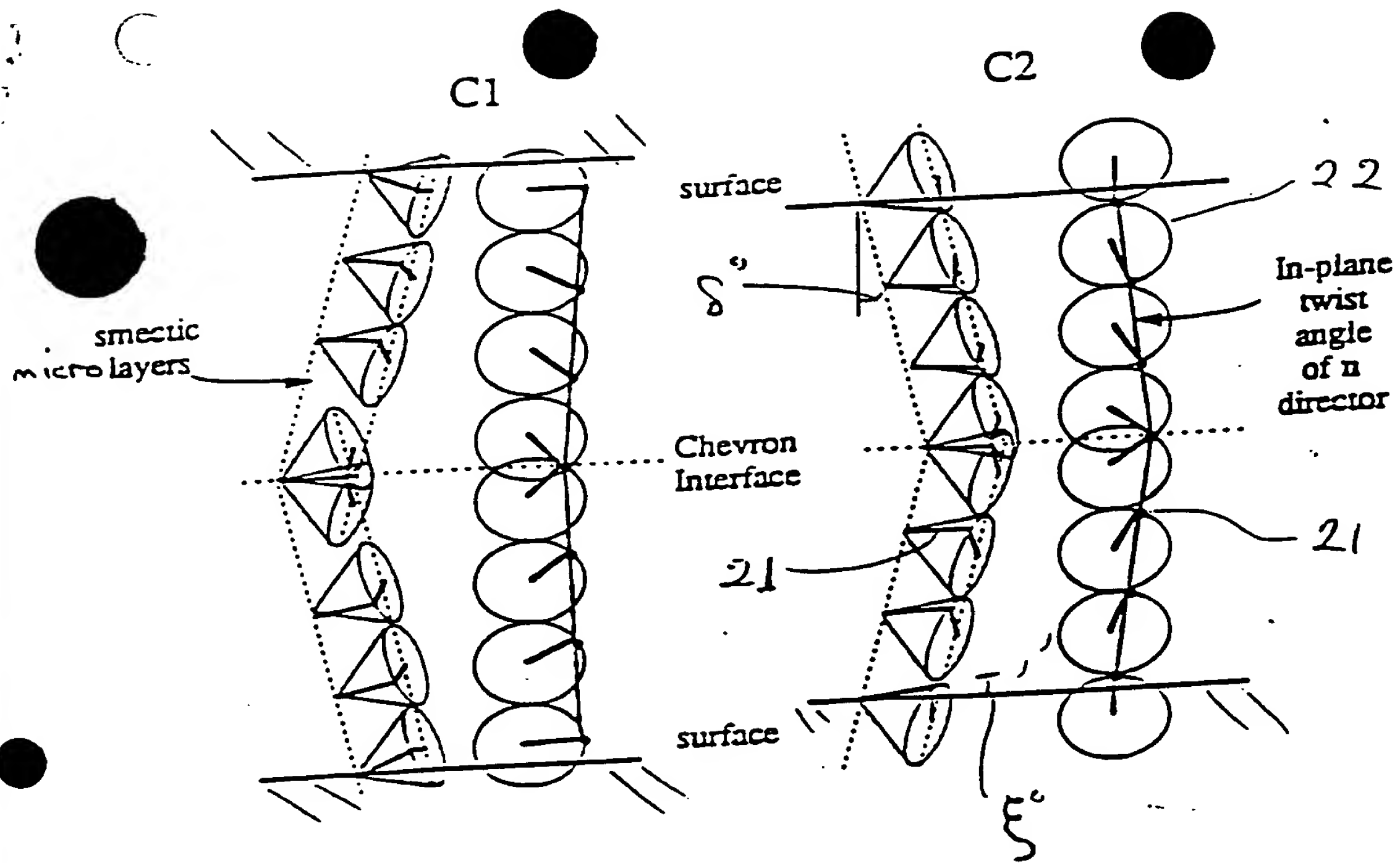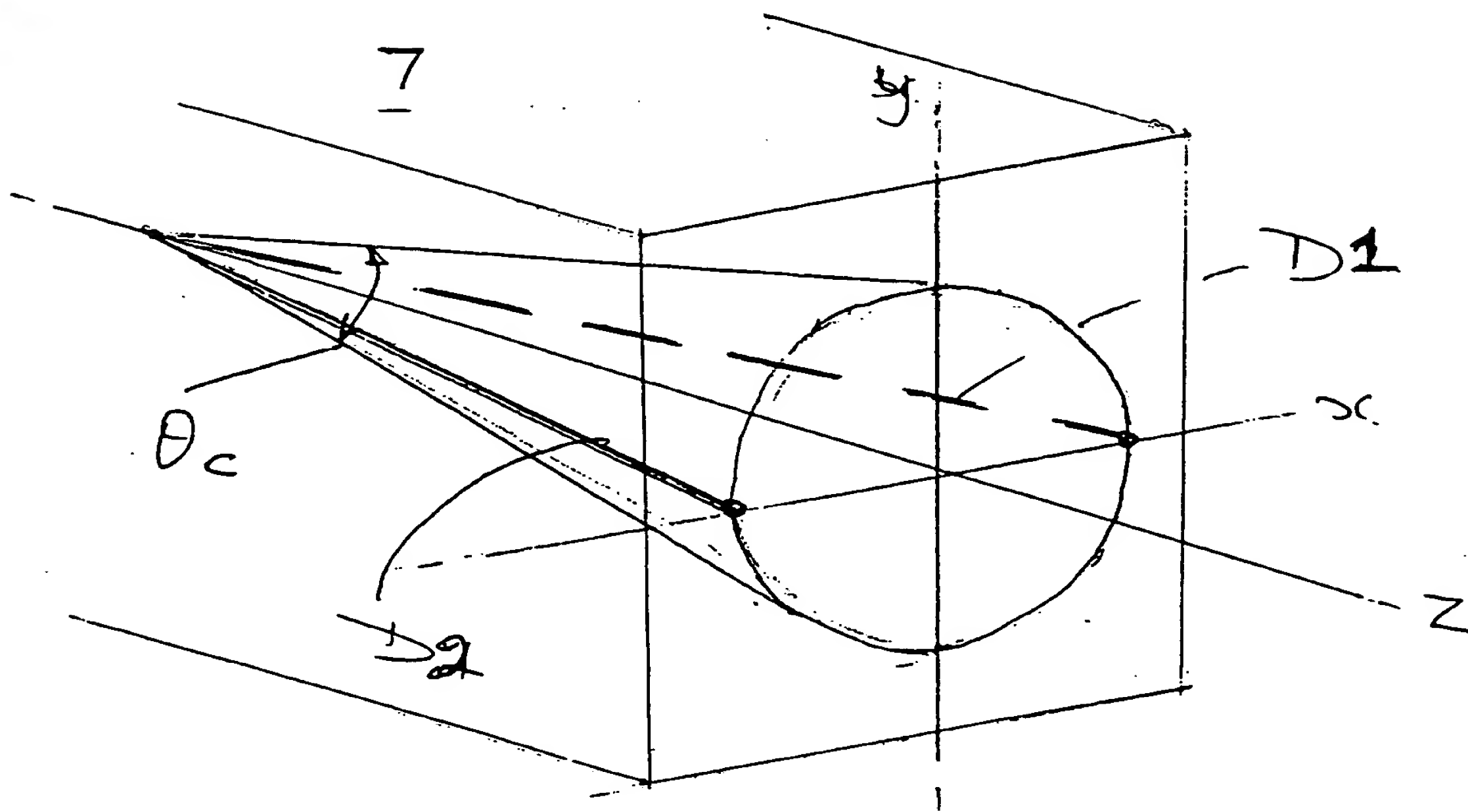
Fig.1.

Fig.2.

C1

C2

surface

smectic
micro layers

Chevron
Interface

21

surface

δ°

21

22

In-plane
twist
angle
of n
director

ξ°

FIG 3

FIG 4

7

θ_c

D1

y

x

z

D2

FIG 5

Legend:
- ——— ZLI 5014 (strong anchoring)
- - - - - 4% N65 in ZLI 5014 (Weak anchoring)

Y-axis: Memory angle (°), from 10 to 50

X-axis: Voltage, from 0 to 14
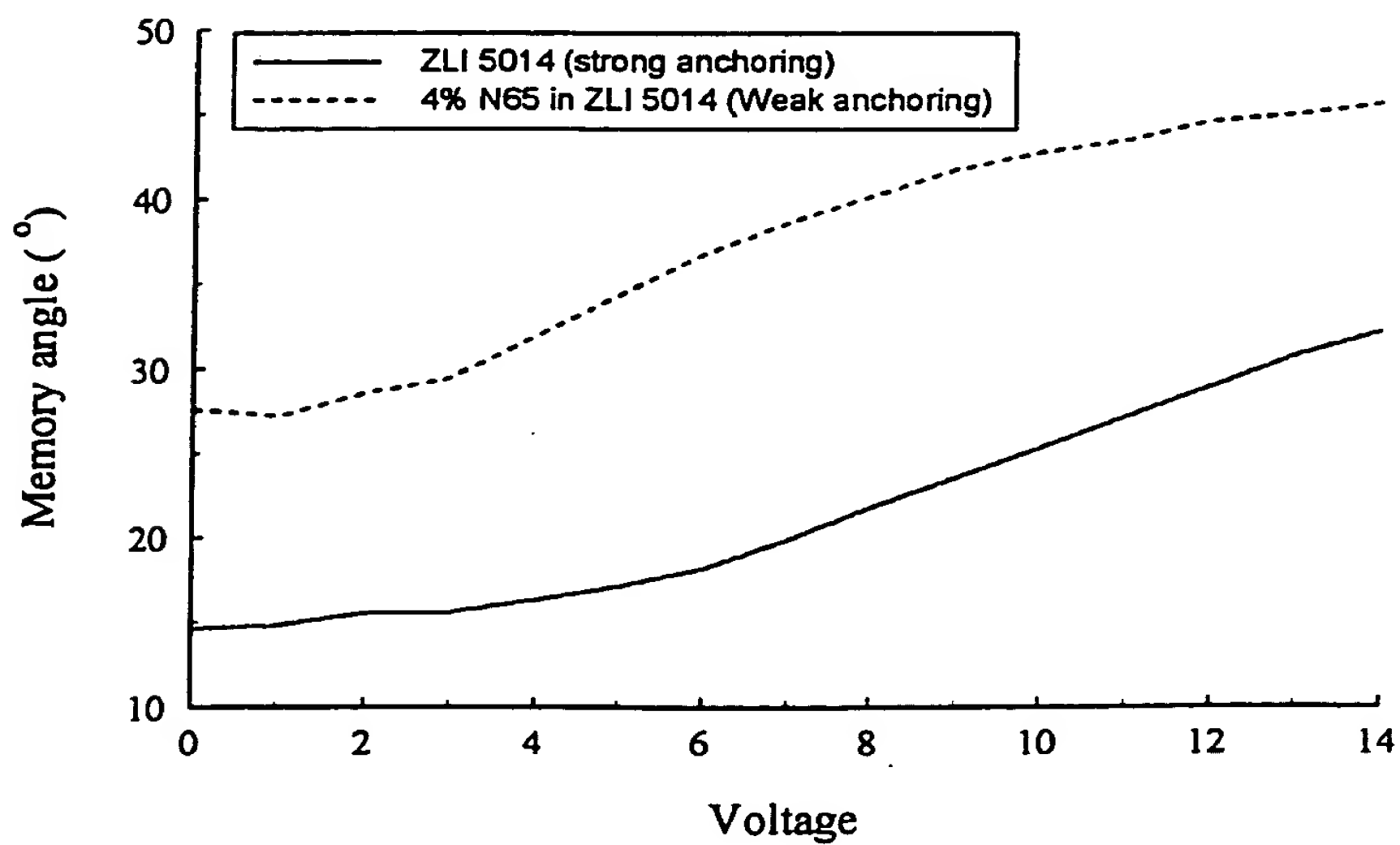
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